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## FUNGAL PEPTAIBIOTICS: ASSESSING POTENTIAL METEORITIC AMINO ACID CONTAMINATION.

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**Introduction:** The presence of non-protein  $\alpha$ -dialkyl-amino acids such as  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB) and isovaline (Iva), which are relatively rare in the terrestrial biosphere, has long been used as an indication of the indigeneity of meteoritic amino acids [1-4]. However, the discovery of  $\alpha$ -AIB in peptides produced by a widespread group of filamentous fungi [e.g., 5,6,7] indicates the possibility of a terrestrial biotic source for the  $\alpha$ -AIB observed in some meteorites. The  $\alpha$ -AIB-containing peptides produced by these fungi are dubbed peptaibiotics.

We measured the molecular distribution and stable carbon and nitrogen isotopic ratios for amino acids found in the total hydrolysates of four biologically synthesized peptaibiotics. We compared these measurements with those from the CM2 carbonaceous chondrite Murchison and from three Antarctic CR2 carbonaceous chondrites in order to understand the peptaibiotics as a potential source of meteoritic contamination.

**Results and Discussion:** Analysis of fluorescently labeled amino acids via liquid chromatography with tandem fluorescence detection and time-of-flight mass spectrometry[8] revealed a range of amino acids in the fungal peptides, with  $\alpha$ -AIB as the dominant component. D-Iva was present in two fungal samples, while L-Iva was absent.

The distribution of amino acids present in the peptaibiotics was much simpler than that seen in the meteorites. The distribution of amino acids is often strikingly complex in meteorites, with acyclic C4 and C5 aliphatic primary amino acids showing complete structural diversity while the corresponding distributions in the fungal peptides consist primarily of  $\alpha$ -AIB and Iva. These distinct distributions provide a way to evaluate the likelihood of terrestrial contamination as a source of meteoritic amino acids.

The compound-specific carbon and nitrogen stable isotopic values for the amino acids in the peptaibiotics were measured via gas chromatography coupled with quadrupole mass spectrometry and isotope ratio mass spectrometry. These isotopic ratios were significantly lighter than those found in the meteorites. In addition, linear regression analysis revealed correlations between the stable isotopic compositions of the amino acids  $\alpha$ -AIB, Gly, and L-Ala in the peptaibiotics. These correlations can be compared with meteoritic data as another tool to rule out terrestrial contamination, although they are insufficient to prove the presence of contamination. Analyses of more peptaibiotics are needed to determine if these correlations are broadly applicable. Similarly, additional compound-specific isotopic analysis of meteoritic amino acids could aid in determining the source of amino acids in meteorites and help elucidate abiotic formation pathways.

**References:** [1] Martins Z. et al. (2007) *Met. Plan. Sci.*, 42, 1581-1595. [2] Ehrenfreund P. et al. (2001) *PNAS*, 98, 2138-2141. [3] Cronin J. R. et al. (1979) *Science*, 206, 335-337. [4] Kvenvolden K. et al. (1970) *Nature*, 288, 923-926. [5] Brückner H. et al. (2009) *Chem Biodivers*, 6, 38-56. [6] Kenner G. W. & Sheppard R. C. (1958) *Nature*, 181, 48-48. [7] Daniel J. F. D. & Rodrigues E. (2007) *Nat. Prod. Rep.*, 24, 1128-1141. [8] Glavin D. P. & Dworkin J. P. (2009) *PNAS*, 106, 5487-5492.